POLAROGRAPHY IN LIQUID AMMONIA

BY

CARLYLE EDWARD SHOEMAKER

B.Ch.E., The Ohio State University, 1943

M.S., University of Illinois, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
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INTRODUCTION

In previous work by Laitinen and Nyman (4, 5), the reduction of the alkali metals at a dropping mercury electrode in liquid ammonia was studied. The half-wave potentials were reported with respect to a lead, 0.1 N lead nitrate electrode since it is an easily reproduced and reliable half-cell reference. During the measurements of the half-wave potentials, a mercury pool anode was used as a reference electrode since no means of providing a simple, direct measurement to the lead electrode could be provided. The difficulty is an experimental rather than a theoretical one and consists of providing a low resistance solution junction with the lead, 0.1 N lead nitrate electrode without allowing lead ions to enter the cathode compartment where they are easily reduced, causing an interference with other reduction processes. The mercury pool anode was shown to be a reproducible reference electrode but it was never characterized with regard to the nature of the potential-determining reaction. By a separate experiment, the mercury pool electrode versus the lead, 0.1 N lead nitrate electrode was established.

The conventional type of dropping mercury electrode, which became plugged easily in liquid ammonia, provided another source of experimental difficulty which occupied a considerable amount of time.

EXPERIMENTAL

The design and construction of the apparatus was different in many details from that previously described. The apparatus was mounted on a corner of a desk over a sink to provide ease of accessibility for operation or modification and repair. A pyrex electrode was made from 0.5 mm capillary tubing by constricting a small portion. The electrode was cut below this portion to provide a somewhat larger and tapering exit. Very little difficulty was experienced with this electrode. To exclude the effect of water, special attention was given to the preparation of anhydrous salts.

DISCUSSION OF RESULTS

The potential of the mercury pool anode was studied by use of a reference or pilot ion whose half-wave reduction potential did not shift in the presence of a wide variety of anions and complexing agents. Thallous ion was selected because it fitted these qualifications in water solution. It was found to be reduced in a one-electron process in liquid ammonia, yielding thallium amalgam.

After electrolysis with a divided cell, it was found by chemical methods that mercuric ions were formed at the anode and that the presence of chloride, nitrate and iodide ions did not shift the potential of the anode, indicating that the mercuric salts of these anions are strong electrolytes in liquid ammonia. The presence of water, which acts as a weak acid also does not affect the anode potential thus ruling out the formation of hydroxy compounds or hydroxy cations of mercury. The mercuric salts formed at the anode do not mix well with the rest of the solution apparently because of the high density of the solution formed. Since the concentration of mercuric ions in contact with the mercury pool is the potential determining factor a stable anode may be prepared by addition of mercuric salt, or by electrolysis. If an appreciable concentration of mercuric ions is present, the residual current will be high and the potential to be accurately known must be measured. If no concentration of mercuric ions is initially present at the anode, after two or three polarograms the anode potential will not change more than 0.01 volt during the remainder of the experiment.

The normal potential of the mercury, mercuric ion electrode was calculated from the potential of the various electrodes and the value calculated from the potential of the electrode corresponding to the most dilute and most accurately known concentration of mercuric ion agreed well with previously measured values by Pleskov (7).

The reduction of the ammonium ion to the amalgam was found to be a reversible one electron process. The half-wave reduction potential was very near to that of sodium. As in the case of the alkali metals, the diffusion currents were found to be somewhat higher than those calculated from the conductance data of Franklin, Kraus, Pleskov and Monosson (2, 3, 6).

Copper was found to be reduced in two steps as are the copper ammonia complexes in water solution. Both steps were reversible and the diffusion currents calculated from the data of Franklin (1) agreed very closely with observed values. The difference between the half-wave potential and the normal potential of the ammine complexes in water solution at 25° was used to calculate the normal potential of the copper, cuprous ion electrode in liquid ammonia. The calculated value did not agree with previously measured values of Pleskov (7). The fact that a correction could not be made for the difference in temperature may partly explain the disagreement.

The observed values of the diffusion currents of thallous ion were found to be in essential agreement with those calculated from the conductance data of Franklin and Kraus (3).

The reduction of oxygen in liquid ammonia was found to be analogous to the process in water solution with the exceptions that the slopes of both waves approached more nearly the values calculated for reversible processes, and the potential of the first wave was found to be dependent to some extent on the acidity.

SUMMARY

1. A new type of dropping mercury electrode which was found to perform satisfactorily in liquid ammonia has been developed.

2. The mercury pool anode has been studied and characterized with respect to its potential and the nature of the potential-determining reactions.

3. The reduction of thallous, cupric ammonium ions and oxygen at the dropping mercury electrode have been studied in liquid ammonia.

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VITA

The author was born on February 19, 1923 in Columbus, Ohio. He attended the public schools of Columbus and Union County, Ohio, until his graduation from Jerome Rural High School in May, 1940. In September of 1940, he entered The Ohio State University, Columbus, Ohio, and received the degree of Bachelor of Chemical Engineering in December, 1943. From January, 1944, until September, 1945, he was employed at the University of Illinois as a research assistant under a National Defense Research Committee contract. The project consisted of the development of smoke munitions and the author was transferred occasionally to Victor Chemical Co., Chicago Heights, for pilot plant operations. In September, 1945, he entered the Graduate School of the University of Illinois. At that time he held a research assistantship in the analytical division of the synthetic rubber research program of the Office of Rubber Reserve until he received the degree of Master of Science in Chemistry in August, 1946. From September, 1946 until graduation he held a teaching assistantship in Inorganic Chemistry.

The author is a member of the American Chemical Society, Tau Beta Pi, Phi Lambda Upsilon, Sigma Xi and Alpha Chi Sigma.

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